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Prediction of MAX phases, $V_{N+1}SiC_N$ ($N=1,2$), from first-principles theory

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We have investigated the phase stability of two MAX phases, V_3SiC_2 and V_2SiC , by means of first-principles total-energy calculations within the generalized-gradient approximation and the projector-augmented wave method. The theoretical bulk modulus of V_3SiC_2 is 219 GPa, which is $\sim 17\%$ larger than that of Ti_3SiC_2 (187 GPa). The total-energy calculations show that V_2SiC is stable with a formation energy of about 0.27 eV/f.u. and that V_3SiC_2 is metastable (only 0.02 eV/f.u. is required to stabilize this phase from its competing phases). We suggest that both these two MAX compounds should be possible to synthesize as stable (or metastable) phases using, e.g., thin-film deposition. © 2007 American Institute of Physics. [DOI: 10.1063/1.2405721]

INTRODUCTION

In recent years a group of inorganic nanolayered compounds with chemical formula $M_{N+1}AX_N$ (hence named MAX phases), where $N=1,2,3$, M is an early transition metal, A an A-group element, and $X=C$ or N , has become the subject of intensive studies.¹⁻³ The MAX phases have remarkable physical properties, such as good electrical conductivity,⁴ exceptional shock resistance and damage tolerance,^{5,6} high loss factor,⁴ fully reversible plasticity,^{4,7} negligible thermopower, and high thermal conductivity.^{4,8} These unique properties make them potentially interesting for applications. Until now most MAX compounds have composition of M_2AX (211, in short).¹ Although much attention has been paid to the prototype Ti_3SiC_2 , more MAX phases with formula M_3AX_2 (312, in short) with superior physical properties remain to be explored. Our recent theoretical simulations have shown that the mechanical properties of M_3SiC_2 crystals are determined primarily by the MC layers.⁹ The hardness of the MC component largely determines the stiffness of the MAX crystal. Since VC is much harder than TiC ,¹⁰ V_3SiC_2 is expected to be a stiffer material than Ti_3SiC_2 . However, until now there is little known about compounds in the $V-Si-C$ system.^{11,12}

The phase diagram of the $V-Si-C$ system was investigated by Schuster and co-workers.^{11,12} The ternary V -based MAX phases are competing with the binary compounds VC , SiC , and V_5Si_3 , as shown in Fig. 1. Here we report the results of the first-principles calculations for the two ternary compounds, V_3SiC_2 and V_2SiC . The stability of the ternary compounds with respect to their competing binary phases is investigated by means of first principles total energy calculations. The crystal structures and the mechanical and electronic properties are also presented here.

DETAILS OF CALCULATIONS

Theoretical calculations were carried out using the first-principles molecular-dynamics code VASP (Vienna *ab initio* simulation program)^{13,14} with the generalized-gradient approximation (GGA) and projector-augmented wave (PAW)

potentials.^{15,16} The electronic wave functions were sampled on a $12 \times 12 \times 4$ mesh or 69 (57) k points in the Brillouin zone¹⁷ (BZ) for V_3SiC_2 (V_2SiC), a $24 \times 24 \times 16$ mesh or 549 k points for SiC , and on a $24 \times 24 \times 24$ mesh or 413 k points for VC (with the NaCl-type structure). For V_5Si_3 an $8 \times 8 \times 6$ mesh with 40 k points was employed in the BZ. For all the calculations the kinetic energy cutoff on the wave functions was 500 eV. The cutoff energy for the augmentation wave functions was 604 eV. Convergence of the total energy with the number of k points and the plane-wave cutoff has been checked. Full relaxation of both lattice parameters and coordinates of atoms is performed for fixed volumes. The equilibrium volume and bulk modulus were calculated by a fit of the volume-energy curves using Murnaghan's equation of state.¹⁸

CALCULATED RESULTS AND DISCUSSION

The calculated results involved the ratio of lattice parameters c/a , equilibrium volume, atomic coordinates, bulk modulus, and formation energy, and they are listed in Table I. We will return below to how the formation energy was calculated. In the table we also compare our results for V_3SiC_2 and V_2SiC with the previously calculated values for Ti_3SiC_2 and Ti_2SiC . A schematic plot of the crystal structures of the two types of MAX phases (the 211 and 312 phases) is shown in Fig. 2. For Ti_3SiC_2 the calculated lattice parameters and atomic coordinates are found to be in good agreement with the experiments.^{1,7} The calculated volume is slightly larger

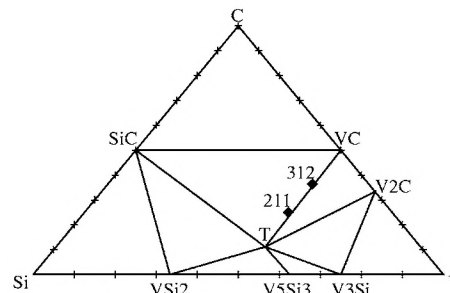


FIG. 1. The phase diagram of the $V-Si-C$ ternary at 1573 K [after Fukai *et al.* (Ref. 12)].

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TABLE I. The calculated results for the $M_3\text{SiC}_2$ and $M_2\text{SiC}$ ($M=\text{Ti}, \text{V}$) compounds using the DFT-GGA method. All the phases have the same space group $P6_3/mmc$ (No. 194). In the structure of (α)- $M_3\text{SiC}_2$, M1 at 2a (0,0,0), M2 at 4f (1/3,2/3, z_M), Si at 2b (0,0,1/4), and C at 4f (1/3,2/3, z_C). β - $M_3\text{SiC}_2$ with Si at 2d (1/3,2/3,1/4). In the structure of $M_2\text{SiC}$, M at 4f (1/3,2/3, z_M), Si at 2d (1/3,2/3,1/4), and C at 2a (0,0,0).

	c/a	z_M	z_C	V (\AA^3)	B (GPa)	δE (eV/f.u.)
Ti_3SiC_2	5.7823	0.1340	0.9279	146.80	187	0.03
	5.7811 ^a	0.135 ^a	0.932 ^a	143.50 ^a	190 ^b	
				206		
β - Ti_3SiC_2	6.1464	0.1243	0.9312	155.50		0.98
V_3SiC_2	6.0150	0.1318	0.9295	129.06	219	0.02
β - V_3SiC_2	6.2093	0.1245	0.9309	134.77		0.46
Ti_2SiC	3.9420	0.0919		103.81	180	-0.20
V_2SiC	4.0553	0.0929		90.62		-0.27

^aReference 7.

^bReference 19.

^cReference 20.

than the experimental data, which is not atypical for this kind of first principles calculations, using GGA. The volume of V_3SiC_2 is calculated to be smaller than that of Ti_3SiC_2 . A slightly larger c/a is found for V_3SiC_2 as compared to that of Ti_3SiC_2 . Correspondingly V_2SiC also has a smaller volume and larger c/a ratio than the corresponding values of Ti_2SiC . The bulk modulus for Ti_3SiC_2 is calculated to be 187 GPa, which is close to the somewhat scattered experimental data, shown in Table I. The bulk modulus is calculated to be about 219 GPa for V_3SiC_2 , which is about 17% larger than that of Ti_3SiC_2 . This trend agrees with the calculated trend of the bulk modulus for the parent compounds, i.e., TiC (~ 260 GPa) and VC (~ 310 GPa).

Structural optimizations have been performed for the binary components V_5Si_3 , SiC, and VC. V_5Si_3 has a hexagonal structure with optimized lattice parameters $a=7.1258$ \AA , $c=4.8180$ \AA , and $V=211.87$ \AA^3 . The lattice parameters are slightly smaller than the experimental values $a=7.161$ \AA and $c=4.762$ \AA for $\text{V}_5\text{Si}_3\text{C}$.¹² It should be noted here that experimentally the latter phase is always found to be substoichiometric and the true chemical formula should read $\text{V}_5\text{Si}_3\text{C}_x$ (with $x < 1$). The small disagreement between theory and experiment for this phase is most likely due to the calculation for simplicity is made for a stoichiometric sample. The layered hexagonal structure of SiC is calculated to have lattice parameters of $a=3.0910$ \AA and $c=5.0759$ \AA , in good agreement with the experimental data. For VC the lattice param-

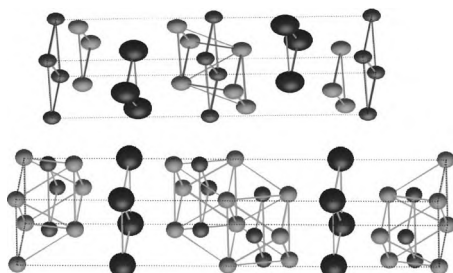


FIG. 2. Crystal structure of $M_2\text{SiC}$ [(a) left] and $M_3\text{SiC}_2$ [(b) right]. The big black balls represent the Si atoms, the small black balls the C atoms, and the light small balls the M atoms.

eter is calculated to be 4.1579 \AA , in good agreement with the experiment and previous theoretical calculations.⁹

The phase stability of the different MAX phases was calculated using the following formula:

$$\delta E_{\text{V}_3\text{SiC}_2} = E_{\text{V}_3\text{SiC}_2} - [7E_{\text{VC}} + (E_{\text{V}_5\text{Si}_3} + E_{\text{SiC}})]/4, \quad (1)$$

$$\delta E_{\text{V}_2\text{SiC}} = E_{\text{V}_2\text{SiC}} - [3E_{\text{VC}} + (E_{\text{V}_5\text{Si}_3} + E_{\text{SiC}})]/4. \quad (2)$$

If the calculated value is negative, the corresponding MAX phase has a lower total energy than the competing phases in the ternary phase diagram [as can be seen in Eqs. (1) and (2) these phases are VC, V_5Si_3 , and SiC] and one would expect the MAX phase to be a stable phase. From our theoretical calculations we obtain $\delta E_{\text{V}_3\text{SiC}_2} = 0.02$ eV/f.u. and $\delta E_{\text{V}_2\text{SiC}} = -0.27$ eV/f.u. From this we draw the conclusion that the 211 phase is stable and that the 312 phase is unstable, but only with a very small energy. Hence, it is not unlikely that also the 312 phase should be possible to stabilize as a meta-stable compound.

Since there is some ambiguity concerning what phases to treat as competing phases in the ternary phase diagram we also investigated the phase stability of the 211 and 312 phases with respect to VC, VSi_2 , and V_5Si_3 . From the formulas

$$\delta E_{\text{V}_3\text{SiC}_2} = E_{\text{V}_3\text{SiC}_2} - [2E_{\text{VC}} + (E_{\text{V}_5\text{Si}_3} + 2E_{\text{VSi}_2})]/7, \quad (3)$$

$$\delta E_{\text{V}_2\text{SiC}} = E_{\text{V}_2\text{SiC}} - [E_{\text{VC}} + (E_{\text{V}_5\text{Si}_3} + 2E_{\text{VSi}_2})]/7, \quad (4)$$

we obtained $\delta E_{\text{V}_3\text{SiC}_2} = 0.01$ eV/f.u., and $\delta E_{\text{V}_2\text{SiC}} = -0.27$ eV/f.u., i.e., values which are very close to the results from Eqs. (1) and (2). For reason of comparison, similar calculations have been performed for the ternary MAX phases in the Ti-Si-C system, in which the ternary compounds are competing with TiC, Ti_5Si_3 , and TiSi_2 .²¹ The differences of the cohesive energies of these ternary MAX phases relative to their competing phases are listed in Table I. The present calculations show that Ti_2SiC is stable compared with the competing binaries TiC, Ti_5Si_3 , and TiSi_2 , by about 0.20 eV/f.u., and compared to the competing phases Ti_3SiC_2 and TiC, by about 0.23 eV/f.u. This finding is in agreement with the former theoretical results by Palmquist *et al.*²¹ who concluded that Ti_2SiC is more stable (about 0.008 eV/at.) than the competing binary phases (Ti_3SiC_2 , Ti_5Si_3 , TiC, and TiSi_2). Table I also shows that Ti_3SiC_2 is unstable, but only with a small energy, 0.02 eV/f.u., compared to the competing phases. It is notable that experimentally Ti_3SiC_2 bulk samples have been prepared, while Ti_2SiC bulk remains to be prepared. Based on this fact, and that the phase stabilities of the Ti-based and V-based systems are rather similar, we conclude that it is not unlikely that V-based MAX phases with 211 and 312 compositions should be possible to stabilize.

Another polymorphic (β -) $\text{Ti}_{n+1}\text{AX}_n$ ($n \geq 2$) phases with a previous structure being named (α -) form were suggested by Farber *et al.*²² and later confirmed by other groups.^{23,24} The difference between the α - and β - $\text{Ti}_{n+1}\text{AX}_n$ is that the A atoms occupy the 2b Wyckoff sites with the fractional coordinates (0,0,1/4) in the α form while in the β phase the A

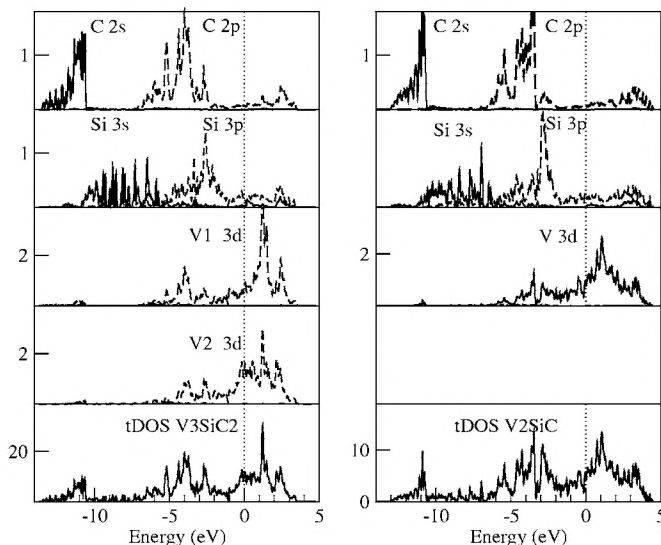


FIG. 3. Partial and total DOSs for V_2SiC (right) and V_3SiC_2 (left).

atoms occupy the $2d$ sites with the fractional coordinates $(1/3, 2/3, 1/4)$. Theoretical analysis found that the β - $Ti_{n+1}AX_n$ structures are less favored than the α form.^{25–27} β - $Ti_{n+1}AX_n$ structures might be stabilized at high pressure²⁶ or high temperature.²⁷

Total-energy calculations have been performed for β - V_3SiC_2 , as well as β - Ti_3SiC_2 for the sake of comparison. The calculated results are included in Table I. The calculations show that β - Ti_3SiC_2 has a slightly shorter a axis, longer c axis, and larger c/a ratio, the same as found in the previous work.²⁵ α - Ti_3SiC_2 is much more stable than β - Ti_3SiC_2 , in line with the former theoretical work.^{25–27} The length of the a axis of β - V_3SiC_2 is calculated to be about 2.9266 Å, which is slightly larger than that (2.9158 Å) of the α form while the c axis (18.1717 Å) of β - V_3SiC_2 is much longer than that (17.5248 Å) of the α phase. The calculations also show that α - V_3SiC_2 is much more stable. Similar to the case of Ti_3SiC_2 , if β - V_3SiC_2 is to be found it is probably a high-temperature or high-pressure phase.

Figure 3 shows for completion the partial and total densities of state (DOSs) for V_3SiC_2 and V_2SiC . A similarity between the DOSs of the two ternary compounds can be easily recognized. The DOS curves form continuous states from about -13.5 (-13.0) to about 3.5 (4.5) eV for V_3SiC_2 (V_2SiC). It is easily recognized that the V $3d$ partial DOS in V_2SiC is quite similar to that of the $3d$ projected V_1 atoms in V_3SiC_2 , i.e., the V atoms in the 312 compound that have similar chemical environment to the V atoms in the 211 compound. In both compounds, the semicore (C $2s$ and Si $3s$) electrons have rather broad bands. In the middle of the energy band, the Si $3s$ states are located with a band that is rather broad (about 5.0 eV) for both compounds. The covalent

chemical bonding in the ternary carbides originates mainly from the interaction (hybridization) between the V $3d$ and the p states of C and Si.

In summary first-principles calculations have been performed for the stability and physical properties of V_3SiC_2 and V_2SiC . It is predicted that V_2SiC is stable at ambient conditions and V_3SiC_2 is close to being stable. V_3SiC_2 is predicted to have a bulk modulus of $\sim 17\%$ larger than the well-known Ti_3SiC_2 compound. It is likely that V_2SiC and V_3SiC_2 are possible to be prepared by techniques such as thin-film deposition.

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